Supporting Information

Ultrasensitive Photoelectrochemical Platform with Micro-emulsion-based p-type Hollow Silver Iodide Enabled by Low Solubility Product (K_{sp}) for H_2S Sensing

Solid AgI preparation

$AgNO_3$ (0.3 g) was dissolved in 6 mL ultrapure water to obtain $AgNO_3$ aqcueous solution (0.3 M, 6 mL), and then KI aqueous solution (0.3 M, 6 mL) was slowly added to realize a deposition reaction. The resultant products were alternately washed several times with ethanol and ultrapure water *via* centrifugation at 10,000 rpm for 5 min, followed by freeze drying.

Characterization

The X-ray powder diffraction (XRD) measurement of the samples was performed on an XRD-7000 with Cu Kα source radiation at a scanning rate of 2° min^{-1} from 10° to 80° (Shimadzu, Japan). The morphologies and structure characterizations were taken with JEOL-7800F fieldemission scanning electron microscopy (FESEM) equipped with INCA X-Max 250 energy-dispersive X-ray spectroscopy (EDS), and JEM-2100 transmission electron microscope, (Japan Electron Optics Laboratory Co., Japan). The X-ray photoelectron spectroscopy (XPS) analysis was measured on Thermo ESCALAB 250Xi spectrometer with a light source of Al Ka X-ray (1486.6 eV) (Thermoelectricity Instruments, U.S.A.). UV–vis diffuse reflectance spectrum was measured on Hitachi U-4100 using with $BaSO_4$ as reference materials (Hitachi, Ltd., Japan). CHI 760E electrochemical workstation was applied for electrochemical and PEC measurements in 0.1 M Na_2SO_4 electrolyte solution in a three-electrode quartz cell (Shanghai Chenhua Instruments Co., China). The three-electrode quartz cell was executed using a platinum wire as counter electrode, a modified glassy carbon electrode (GCE, Φ = 3 mm) as working electrode, and a saturated calomel electrode (SCE) for electrochemical measurement or a Ag/AgCl for PEC measurement as reference electrode. LED light source of PEAC 200A (Tianjin AiDa Hengsheng Technology Co., Ltd., China) and Xe lamp parallel light source system of CHF-XM35-500W (Beijing Trusttech Co. Ltd., China) were applied.

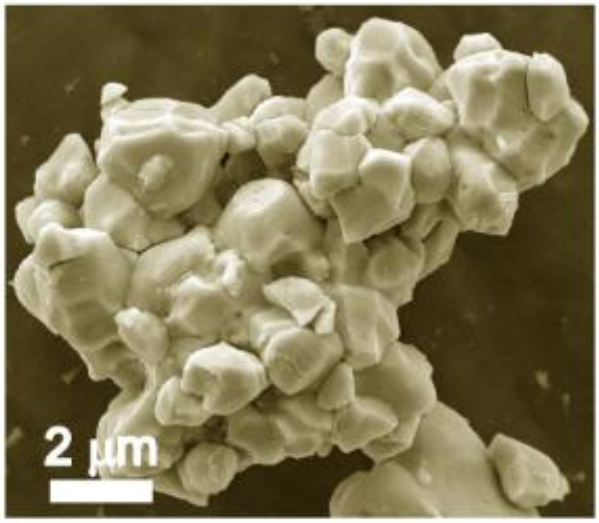

Figure S1. FESEM image of solid AgI.

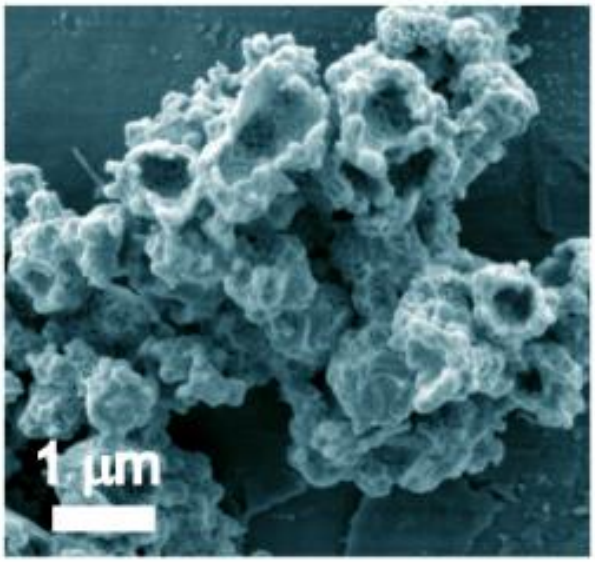

Figure S2. FESEM image of hollow AgI.

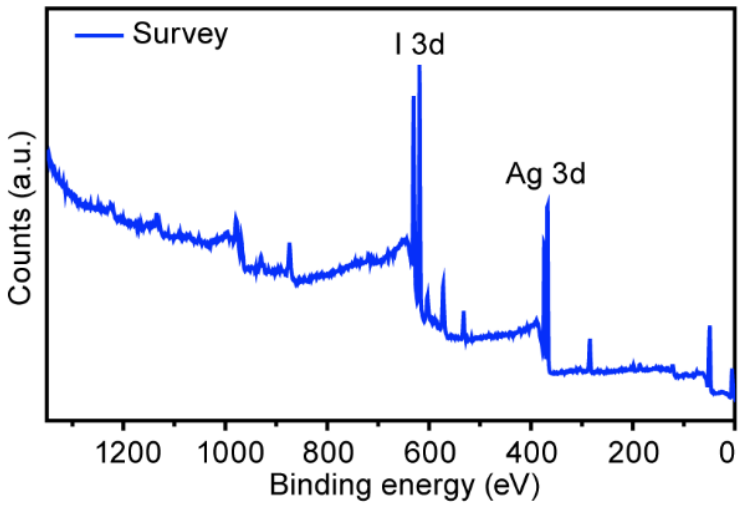

Figure S3. The survey XPS spectrum of hollow AgI.

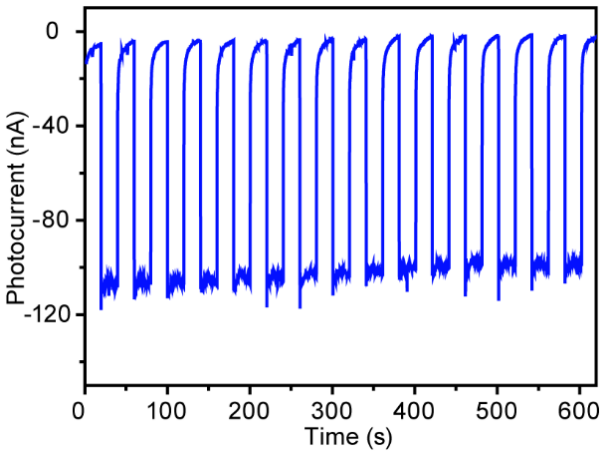

Figure S4. The stability of proposed PEC platform after hydrogen sulfide sensing.

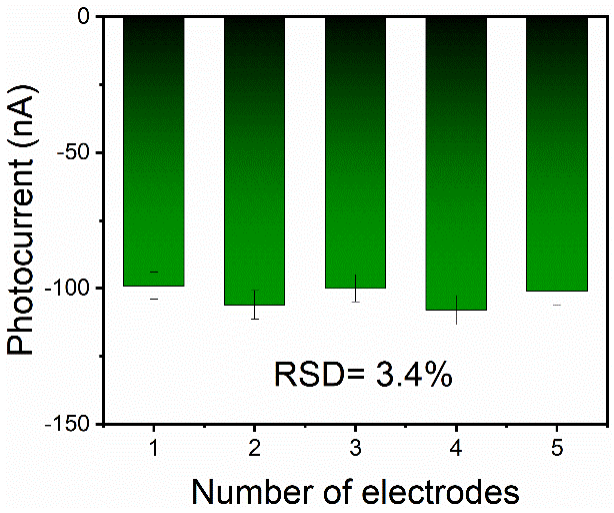

Figure S5. The photocurrent responses of the five-paralleled modified photoelectrodes in phosphate buffer (0.1 M, 10 mL, pH=7.0).

Table S1. Comparison with reported hydrogen sulfide sensing.

Method	Dynamic range	Detection limit	References
Fluorescence	0-50 μM	0.25 nM	[1]
Fluorescence	0-500 μM	0.22 μM	[2]
Colorimetric	2.05 μM-65.75 μM	0.993 μM	[3]
Colorimetric	0-80 μM	0.5 μM	[4]
Electrochemiluminescent	0.1 nM-10 μM	1.7 pM	[5]
Electrochemiluminescent	0.5 μM-10 μM	0.25 μM	[6]
Electrochemistry	0.1 nM-500 nM	0.04 nM	[7]
Electrochemistry	0.08 μM−0.38 μM	0.038 μM	[8]
Photoelectrochemistry	1 pM −10 nM	0.36 pM	[9]
Photoelectrochemistry	5 μM - 100 μM	1.67 μM	[10]
Photoelectrochemistry	10 nM −100 nM	10 nM	[11]
Photoelectrochemistry	10 nM−1 mM	0.7 nM	[12]
Photoelectrochemistry	0.1 fM-10 nM	0.04 fM	This work

Table S2. Recovery tests of the as-prepared cathode PEC sensing platform for H_2S measurement.

Added H_2S concentrations (nM)	H_2S concentrations (nM)	Recovery (%)
0.031	0.032	103.2
0.151	0.145	96.03
2.32	2.406	103.7
8.24	8.418	102.2

References

[1] Karakus, E.; U ¸cu ¸ncü, M.; Emrullahoglu, M. Electrophilic Cyanate As a Recognition Motif for Reactive Sulfur Species: Selective Fluorescence Detection of H_2S, Anal. Chem. 88 (2016) 1039-1043.

[2] Luo, W.F.; Xue, H.Y.; Ma, J.J.; Wang, L.; Liu, W.S. Molecular Engineering of a Colorimetric Two-photon Fluorescent Probe for Visualizing H_2S Level in Lysosome and Tumor. Anal. Chim. Acta 1077 (2019) 273-280.

[3] Kim, T.J.; Lee, Y.J.; Ahn, Y.J.; Lee, G.J. Characterization of H_2S Releasing Properties of Various H_2S Donors Utilizing Microplate Cover-based Colorimetric Assay, Anal. Biochem. 574 (2019) 57–65.

[4] Zeng, J.B.; Li, M.; Liu, A.; Feng, F.; Zeng, T.; Duan, W.; Li, M.M.; Gong, M.F.; Wen, C.Y.; Yin, Y.D. Au/AgI Dimeric Nanoparticles for Highly Selective and Sensitive Colorimetric Detection of Hydrogen Sulfde, Adv. Funct. Mater.28 (2018) 1800515.

[5] Huang, J.; Qu, W.B.; Zhu, J.L.; Liu, H.; Wen, W.; Zhang, X.H.; Wang, S.F. Electrochemiluminescent Sensor Based on $Ru(bpy)_3^{2+}$-doped Silica Nanoprobe by Incorporating a New Co-reactant NBD-amine for Selective Detection of Hydrogen Sulfide, Sensor. Actuat. B-Chem. 284 (2019) 451–455.

[6] Yue, X.X.; Zhu, Z.Y.; Zhang, M.N.; Ye, Z.Q. Reaction-Based Turn-on Electrochemiluminescent Sensor with a Ruthenium(II) Complex for Selective Detection of Extracellular Hydrogen Sulfide in Rat Brain, Anal. Chem. 87 (2015) 1839-1845.

[7] Zhao, Y.; Yang, Y.X.; Cui, L.Y.; Zheng, F.J.; Song, Q.J. Electroactive Au@Ag Nanoparticles Driven Electrochemical Sensor for Endogenous H_2S Detection, Biosens. Bioelectron. 117 (2018) 53-59.

[8] Dhakshinamoorthy, J.; Pullithadathil, B. New Insights Towards Electron Transport Mechanism of Highly Efficient p-Type CuO (111) Nanocuboids-Based H_2S Gas Sensor, J. Phys. Chem. C 120 (2016) 4087−4096.

[9] Li, H.B.; Li, J.; Zhu, Y.Y.; Xie, W.Y.; Shao, R.; Yao, X.X.; Gao, A.Q.; Yin, Y.D. Cd^{2+}-Doped Amorphous TiO_2 Hollow Spheres for Robust and Ultrasensitive Photoelectrochemical Sensing of Hydrogen Sulfide, Anal. Chem. 90 (2018) 5496−5502.

[10] Zeng, H.M.; Liu, Y.L.; Xu, Z.G.; Wang, Y.J.; Chai, Y.Q.; Yuan, R.; Liu, H.Y. Construction of Z-scheme g-C_3N_4/Ag/AgI Heterojunction for Highly Selective Photoelectrochemical Detection of Hydrogen Sulfide, Chem. Commun. 55 (2019) 11940-11943.

[11] Tang, J.; Zhang, Y.Y.; Kong, B.; Wang, Y.C.; Da, P.M.; Li, J.; Elzatahry, A. A.; Zhao, D.Y.; Gong, X.G.; Zheng, G.F. Solar-Driven Photoelectrochemical Probing of Nanodot/Nanowire/Cell Interface, Nano Lett. 14 (2014) 2702−2708.

[12] Ding, L.H.; Ma, C.; Li, L.; Zhang, L.N.; Yu, J. H. A Photoelectrochemical Sensor for Hydrogen Sulfide in Cancer Cells Based on the Covalently and in Situ Grafting of CdS Nanoparticles onto TiO_2 Nanotubes, Electroanal. Chem. 783 (2016) 176−181.